

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



IP
GENERAL ELECTRIC



(43) International Publication Date
16 January 2003 (16.01.2003)

PCT

(10) International Publication Number
WO 03/004542 A1

(51) International Patent Classification: C08F 265/06

(21) International Application Number: PCT/KR01/02274

(22) International Filing Date:
27 December 2001 (27.12.2001)

(25) Filing Language: Korean

(26) Publication Language: English

(30) Priority Data:
2001/39820 4 July 2001 (04.07.2001) KR

(71) Applicant (for all designated States except US): LG
CHEM, LTD. [KR/KR]; LG Twin Tower, Yoido-dong 20,
Youngdungpo-ku, Seoul 150-721 (KR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): SHIN, Yang-Hyun
[KR/KR]; LG Chem, Ltd. Dormitory Gukwan-208,
Ansan-dong 29, Yeocheon-city, Cheollanam-do 555-050

(KR). YOO, Keun-Hoon [KR/KR]; Hanbit Apt. 123-801,
Eocun-dong, Yousong-ku, Daejeon-city 305-755 (KR).
AHN, Tae-Bin [KR/KR]; Ganeung 1-dong 632-21, Ui-
jeongbu-city 480-101 (KR). LEE, Chan-Hong [KR/KR];
Lucky Hana Apt. 102-901, Sinsong-dong, Yousong-ku,
Daejeon-city 305-721 (KR).

(74) Agent: YOU ME PATENT & LAW FIRM; Teheran
Building, 825-33, Yoksam-dong, Kangnam-ku, Seoul
135-080 (KR).

(81) Designated States (national): CN, JP, US.

(84) Designated States (regional): European patent (AT, BE,
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE, TR).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.



WO 03/004542 A1

(54) Title: METHODS FOR PREPARING OF WEATHERABILITY THERMOPLASTIC RESIN

(57) Abstract: The present invention relates to a method for preparing a weatherable thermoplastic resin, and more particularly to a method for preparing a thermoplastic acrylate-styrene-acrylonitrile (ASA) resin having superior weatherability and colorability. In detail, the present invention provides a method comprising the steps of: a) preparing a seed by adding a water-soluble initiator to an aromatic vinyl compound, or to a (meth)acrylic acid alkyl ester, and polymerizing; b) preparing an alkyl acrylate rubber polymer by adding an alkyl acrylate monomer, an emulsifier of pH 3--9, and an oil-soluble initiator to the seed, and polymerizing; and c) preparing a thermoplastic resin by adding an aromatic vinyl compound, a vinyl cyanide compound, an emulsifier of pH 9--13, and an oil-soluble initiator to the alkyl acrylate rubber polymer, and graft polymerizing.

METHODS FOR PREPARING OF WEATHERABILITY**THERMOPLASTIC RESIN****BACKGROUND OF THE INVENTION****(a) Field of the Invention**

5 The present invention relates to a method for preparing thermoplastic resin having weatherability, and more particularly to a method for preparing thermoplastic acrylate-styrene-acrylonitrile (ASA) resin having excellent weatherability and color matching properties.

(b) Description of the Related Art

10 Recently, as the thermoplastic resin industry has advanced and the distinctiveness of goods model has gained popularity, research on giving high function of colorability etc, to materials used in the industry has progressed a great deal.

 In order to increase resin functionality, the prior art has used an
15 acrylonitrile-butadiene-styrene (ABS) copolymer resin. Although ABS resin has good qualities of impact resistance, processibility, and surface gloss, etc., it has a problem in that it is unsuitable for use outdoors due to bad weatherability and light resistance because of properties of the resin, and thermal stability is also bad, chemical resistance is weak, and its properties diminish over time.

20 In order to solve these problems, acrylate-styrene-acrylonitrile (ASA) resin is being developed.

In a method for preparing ASA resin of the prior art, Japanese Laid-Open Patent Publication No. Hei 5-202264 has suggested a method for improving properties by preparing ASA resin with a bimodal shape. The method discloses that ASA resin with a small diameter of 50 ~ 200 nm, and ASA resin with a large
5 diameter of 200 ~ 1000 nm each prepares, and then the two resins are latex blended together, and resultant blends with a separately prepared styrene-acrylonitrile (SAN) copolymer to produce ASA resin having superior weatherability.

However, since the method separately prepares two ASA resins the
10 process is complex, and colorability, surface gloss, and sufficient impact strength are not exhibited. German Patent No. 1260135 has described the method in detail.

In another method, Japanese Laid-Open Patent Publication No. Hei 4-180949 discloses a method for preparing ASA resin by making multi-layer graft
15 copolymer particles. The method suggests a preparation of ASA resin for improving weatherability in which a hard core is first prepared by using a monomer having a high glass transition temperature, then a crosslinked acrylate rubber component is added, followed by a crosslinked shell of a styrene monomer, an acrylonitrile monomer having a high glass transition temperature, and a
20 crosslinking agent, and finally by preparing a soft shell with an uncrosslinked styrene monomer and an acrylonitrile. However, this method also does not

mention a method capable of improving colorability and surface gloss of ASA resin.

As explained, although a general ASA resin has weatherability, chemical resistance, and thermal stability, it has problems of a lowering colorability and surface gloss, weak side impact strength, and its molding capacity is limited due to a low fluidity. Additionally, important technical difficulties to overcome in the preparation of ASA resin are known to be that colorability and surface gloss showing a pearl color etc. while color matching are reduced, and impact strength is low. Also, color dispersion falls due to properties of acrylate rubber.

10

SUMMARY OF THE INVENTION

The present invention is made in consideration of the problems of the prior art, and it is an object of the present invention to provide a method for preparing thermoplastic acrylate-styrene-acrylonitrile (ASA) resin having superior weatherability, as well as properties and colorability equal to ABS resin.

15

It is another object of the present invention to provide a method for preparing thermoplastic resin having superior impact resistance, chemical resistance, and surface gloss.

In order to achieve these objects, the present invention provides a method for preparing a weatherable thermoplastic resin comprising the steps of:

20

a) preparing a seed by adding 0.05-0.2 weight parts of a water-soluble initiator to 0.5-10 weight parts of either an aromatic vinyl compound or a

(meth)acrylic acid alkyl ester,

and polymerizing;

b) preparing an alkyl acrylate rubber polymer by adding

i) 5-45 weight parts of an alkyl acrylate monomer,

5 ii) 1-5 weight parts of an aromatic vinyl compound, a (meth)acrylic acid alkyl ester, or a vinyl cyanide compound,

iii) 0.2-1.0 weight parts of a metal salt derivative of alkyl sulfosuccinate with $C_{12} \sim C_{18}$, or a metal salt derivative of alkyl sulfuric acid ester, or metal salts of sulfonate, with $C_{12} \sim C_{20}$, as an emulsifier, and

10 iv) 0.05-2 weight parts of an oil-soluble initiator to the seed,

and polymerizing; and

c) preparing a thermoplastic resin by adding

i) 10-40 weight parts of an aromatic vinyl compound,

15 ii) 1-20 weight parts of a vinyl cyanide compound,

iii) 0.5-3.0 weight parts of metal salts of rosinate or metal salts of carboxylate, with $C_{12} \sim C_{20}$, as an emulsifier, and

iv) 0.05-0.2 weight parts of an oil-soluble initiator

to the alkyl acrylate rubber polymer, and graft copolymerizing.

20 The present invention also provides a weatherable thermoplastic resin prepared by the above method.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will now be explained in detail.

In order to solve the problem of the method for preparing weatherable
5 resin that lowers colorability and surface gloss of acrylate-styrene-acrylonitrile
(ASA) resin of the prior art, the present inventors continuously studied. As a
result, the present invention was completed by introducing methylmethacrylate, by
controlling contents of each component, by introducing a hard core during
polyacrylate rubber polymerization, and by using a water-soluble initiator and an
10 oil-soluble initiator differently in the polymerization steps to prepare ASA resin.
The resin of the present invention comprises an acrylonitrile giving superior
chemical resistance, an acrylate-based rubber giving superior impact resistance,
and a styrene giving superior processability, to prepare a thermoplastic resin
having superior impact resistance, chemical resistance, processability,
15 weatherability, colorability, and surface gloss.

The method for preparing thermoplastic resin having superior
weatherability of the present invention comprises the steps of a) preparation of a
seed, b) preparation of a crosslinked alkyl acrylate rubber polymer, and c)
preparation of a graft copolymer, and each process is explained in more detail as
20 follows.

a) Preparation of a seed

First, in order to produce a hard core for preparing a crosslinked alkyl acrylate rubber polymer, the present invention prevents distortion of the rubber by hardening a rubber core through seed polymerization of 0.5 to 10 weight parts of an aromatic vinyl compound monomer or a (meth)acrylic acid alkyl ester monomer
5 having a high glass transition temperature, based on 100 weight parts of the total monomers.

Examples of preferable (meth)acrylic acid alkyl ester compounds are (meth)acrylic acid methyl ester, (meth)acrylic acid ethyl ester, (meth)acrylic acid propyl ester, (meth)acrylic acid 2-ethyl hexyl ester, (meth)acrylic acid decyl ester,
10 and (meth)acrylic acid lauryl ester etc., and more preferable is a methyl methacrylate such as (meth)acrylic acid methyl ester.

The aromatic vinyl compound used is a styrene monomer derivative. Preferable examples are selected from the group consisting of styrene, α -methyl styrene, and vinyl toluene, and particularly preferable is styrene.

15 According to the present invention, in the case of initial seed polymerization, a water-soluble initiator is used; and in the case of polymerization in second and third steps, an oil-soluble initiator is used, and thus colorability and surface gloss can be improved by increasing graft efficiency of the reactant. The initiator used in the present invention is an inorganic or an organic peroxide. In
20 the case of seed polymerization, the water-soluble initiator is used to improve colorability, and the oil-soluble initiator is used in the graft and rubber particle

growth reaction. As examples, the water-soluble initiator is preferably selected from the group consisting of potassium persulfate, sodium persulfate, and ammonium persulfate, while the oil-soluble initiator is preferably cumene hydroperoxide, t-butyl hydroperoxide, or benzoyl peroxide.

5 The content of the water-soluble initiator is preferably 0.05 to 0.2 weight parts based on 100 weight parts of total monomers.

 The crosslinking agent used in the present invention is selected from the group consisting of ethyleneglycol dimethacrylate, diethyleneglycol dimethacrylate, triethyleneglycol dimethacrylate, 1,3-buthanediol dimethacrylate, 1,6-hexanediol
10 dimethacrylate, neopentylglycol dimethacrylate, trimethylol propane trimethacrylate, and trimethylol methane triarylate. The content is 0.05 to 0.3 weight parts based on 100 weight parts of total monomers.

 An electrolyte used in the present invention is selected from the group consisting of NaHCO_3 , $\text{Na}_2\text{S}_2\text{O}_7$, K_2CO_3 , and preferable is NaHCO_3 . The content
15 of electrolyte is 0.05 to 0.4 weight parts based on 100 weight parts of total monomers.

b) Preparation of crosslinked alkyl acrylate rubber polymer

 The present invention performs the step of preparing a crosslinked alkyl acrylate rubber polymer by adding an alkyl acrylate monomer; an aromatic vinyl
20 compound, a (meth)acrylic acid alkyl ester, or a vinyl cyanide compound; a metal salt derivative of alkyl sulfosuccinate with $\text{C}_{12}\sim\text{C}_{18}$, or a metal salt derivative of

alkyl sulfuric acid ester or metal salts of sulfonate with $C_{12} \sim C_{20}$, as an emulsifier; and the oil-soluble initiator, to the seed prepared in the a) step.

In the present invention, an alky acrylate monomer (preferably butyl acrylate) as a major monomer is used, and the content thereof is 5 to 45 weight parts based on 100 weight parts of total monomers.

Additionally, the present invention preferably uses 0.1 to 15 weight parts of an optimized mixture ratio of methyl methacrylate, styrene, and acrylonitrile as a supplement to improve efficiency of the rubber particles and the pearl color, and it is also possible to copolymerize a functional monomer. The functional monomer is selected from the group consisting of methacrylic acid, acrylic acid, maleic acid, itaconic acid, and fumaric acid.

An aqueous solution of the emulsifier preferably has pH of 3 ~ 9, and for example the emulsifier used is a metal salt derivative of alkyl sulfosuccinate with $C_{12} \sim C_{18}$, or a derivative of alkyl sulfuric acid ester or metal salts of sulfonate with $C_{12} \sim C_{20}$. The metal salt derivative of alkyl sulfosuccinate with $C_{12} \sim C_{18}$ is a sodium or potassium salt etc. of dioctyl sulfosuccinate, dicyclohexyl sulfonate, or dihexyl sulfosuccinate; and the derivative of alkyl sulfonic ester with $C_{12} \sim C_{20}$ or metal salts of sulfonate can be used as alkyl sulfate metal salts such as sodium lauric sulfate, sodium dodecyl sulfate, sodium dodecyl benzene sulfate, sodium octadecyl sulfate, sodium oleic sulfate, potassium dodecyl sulfate, potassium octadecyl sulfate, etc. Among them, in overall consideration of the graft reaction

of the graft phase for foam occurrence and the drying property of the crosslinked butyl acrylate rubber polymer, sodium dioctyl sulfosuccinate or potassium dioctyl sulfosuccinate is preferable. The content of emulsifier used is 0.2 to 1.0 weight parts based on 100 weight parts of total monomers.

- 5 If a carboxylate metal salt derivative such as a metal salt of aliphatic acid or a metal salt of rosinate etc. where an aqueous solution of the emulsifier has pH of about 9 ~ 13 is used, although drying can be enhanced, it is difficult to graft methacrylic acid methyl in the butyl acrylate rubber polymer into ASA resin due to a lower moisture content, and thus stripping occurs because of phase separation
- 10 resulting in a substantial decrease in impact strength.

The oil-soluble initiator used in the present invention is cumene hydroperoxide, t-butyl hydroperoxide, or benzoyl peroxide. The content is 0.05 to 0.2 weight parts based on 100 weight parts of total monomers.

- Also, according to the preparation of the acrylate rubber polymer of the
- 15 present invention, the b) step can further comprise a grafting agent selected from the group consisting of v) aryl methacrylate (AMA), triarylisocyanurate (TAIC), triarylamine (TAA), and diarylamine (DAA), wherein the content is 0.01 to 0.07 weight parts based on 100 weight parts of total monomers.

- The crosslinking agent used in the present invention is selected from the
- 20 group consisting of ethyleneglycol dimethacrylate, diethyleneglycol dimethacrylate, triethyleneglycol dimethacrylate, 1,3-buthanediol dimethacrylate,

1,6-hexanediol dimethacrylate, neopentylglycol dimethacrylate, trimethylol propane trimethacrylate, and trimethylol methane triarylate. The content is 0.05 to 0.3 weight parts based on 100 weight parts of total monomers.

The electrolyte used in the present invention is selected from the group
5 consisting of NaHCO_3 , $\text{Na}_2\text{S}_2\text{O}_7$, and K_2CO_3 , and NaHCO_3 is preferable. The content of electrolyte is 0.05 to 0.4 weight parts based on 100 weight parts of total monomers.

The reaction can be performed only through emulsion polymerization, or it can be preformed by suitably mixing emulsifier-free emulsion polymerization and
10 emulsion polymerization to prepare acryl rubber polymer latex. The monomers can be added continuously, or by adding continuously and in batches.

The aqueous solution of the crosslinked alkyl acrylate rubber polymer latex after polymerization of the present invention preferably has pH of 5 to 9, and more preferably 6 to 8. The rubber polymer preferably has a diameter of 2500 ~
15 5000 Å, and more preferably 3000 ~ 4500 Å.

c) Preparation of graft copolymer

The present invention can have improved impact strength and it can maintain colorability of ASA resin better when compared to the prior art through the graft reaction by adding an aromatic vinyl compound, a vinyl cyanide
20 compound, metal salts of rosinate or metal salts of carboxylate with $\text{C}_{12}\sim\text{C}_{20}$ as an emulsifier, and an oil-soluble initiator to the acrylate rubber polymer prepared

in the b) step.

The monomer grafted in the crosslinked alkyl acrylate rubber polymer uses 10 to 40 weight parts of the aromatic vinyl compound and 1 to 20 weight parts of the vinyl cyanide compound, and a functional monomer is further used
5 according to necessity.

The aromatic vinyl compound used is a styrene monomer derivative. As an example, it is selected from the group consisting of styrene, α -methyl styrene, and p-methyl styrene, and preferable is styrene. The vinyl cyanide used is acrylonitrile or methacrylonitrile, and preferable is acrylonitrile. The functional
10 monomer possibly used can be methacrylic acid, acrylic acid, maleic acid, itaconic acid, fumaric acid, etc.

The aqueous solution of the emulsifier preferably has pH of 9 ~ 13, and as an example the emulsifier is preferably a metal salt derivative of carboxylate such as a metal salt derivative of aliphatic acid with $C_{12} \sim C_{20}$, a metal salt of
15 rosinate, etc. The metal salt derivative of aliphatic acid is a sodium or potassium salt of a fatty acid, lauric acid, or oleic acid, and the metal salt of rosinate is sodium rosinate or potassium rosinate.

If a metal salt derivative of carboxylate such as a metal salt of aliphatic acid with $C_{12} \sim C_{20}$ or a metal salt of rosinate etc. where the aqueous solution
20 emulsifier has a pH of about 9 ~ 13 is used, as the pH of the total system rises little by little, a carboxyl group of butyl acrylate rubber polymer having a low glass

transition temperature comes out of the particle. But as polymerization progresses, a graft phase having a high glass transition temperature comes to the inner part of the butyl acrylate rubber polymer particle, and thus a surface glass transition temperature can be lowered and thereby it can be coagulated at normal pressure, and additionally, drying also becomes easier because the moisture content inside the ASA particle is remarkably decreased.

In the case a graft reaction initiator is used as explained, an oil-soluble initiator such as cumene hydroperoxide, t-butyl hydroperoxide, or benzoyl peroxide is used, and the content is preferably 0.05 to 0.3 weight parts based on 100 weight parts of total monomers.

In the case of the grafting reaction, the mixing monomer comprising an emulsifier is preferably continuously added. With the batch adding method, since pH of the polymerization system rises at the same time, it is difficult to graft and the inner structure is not uniform due to inferior particle stability.

The final latex aqueous solution prepared by the method preferably has pH of 8 ~ 11, and more preferably 9 ~ 10.5. Additionally, a diameter of the rubber polymer latex is preferably 3000 ~ 6000 Å, and more preferably 3500 ~ 4500 Å.

As above, according to the present invention, a weatherable thermoplastic resin which has superior impact resistance, chemical resistance, processability etc., and improved colorability and surface gloss can be obtained

by controlling an amounts of the monomer components such as a (meth)acrylic acid alkyl ester compound, an aromatic vinyl compound, a vinyl cyanide compound etc. added in a polyacrylate-based rubber latex, and particularly by graft polymerizing them together with a water-soluble initiator and an oil-soluble

5 initiator.

The present invention will be explained in more detail with reference to the following Examples. However, these are to illustrate the present invention, and the present invention is not limited to them.

[Examples]

10 First polymerization step

	ion exchange water	70 wt parts
	styrene (SM)	2 wt parts
	ethyleneglycol dimethacrylate (EDMA)	0.02 wt parts
	sodium bicarbonate	0.1 wt parts
15	potassium persulfate (KPS)	0.01 wt parts

The components were introduced into a polymerization reactor under a nitrogen atmosphere, and the temperature was elevated to 70 °C and they were reacted for 1 hour.

Second polymerization step

20	potassium rosinate	45 wt parts
	dioctylsulfosuccinate	0.5 wt parts

	Butylacrylate	40 wt parts
	styrene (SM)	3 wt parts
	methyImethacrylate (MMA)	2 wt parts
	ethyleneglycol dimethacrylate (EDMA)	0.12 wt parts
5	aryImethacrylate	0.04 wt parts
	sodium bicarbonate	0.1 wt parts
	cumene hydroperoxide (CHP)	0.06 wt parts

All the above components except cumene hydroperoxide were mixed in a polymerization reactor, and then the obtained mixture and a catalyst were each

10 continuously introduced to the product of the first polymerization step at 70 °C over 4 hours to conduct the polymerization reaction. The diameter of the obtained latex was 4000 Å, the pH thereof was 8, and a polymerization conversion rate was 98%. The diameter of the latex was measured by the dynamic laser-light scattering method using a Nicomp analyzer (Model: 370HPL).

15 Third polymerization step

	ion exchange water	63 weight parts
	potassium rosinate	0.5 weight parts
	styrene(SM)	38 weight parts
	acrylonitrile(AN)	15 weight parts
20	cumene hydroperoxide(CHP)	0.11 weight parts

All the above components except cumene hydroperoxide were mixed in a

polymerization reactor, and then the obtained mixture and a catalyst were each continuously introduced to the product of the second polymerization step at 70 °C over 4 hours to conduct a polymerization reaction. Thereafter, in order to improve the polymerization conversion rate, the resultant was further reacted at 80 °C for 1 hour, and it was then cooled to 60 °C. The diameter of the obtained latex was 4800 Å, the pH thereof was 9.5, the polymerization conversion rate was 99%, and the graft rate was 45%.

The obtained latex was coagulated at 85 °C, normal pressure with a calcium chloride aqueous solution, then aged at 95 °C, then dehydrated and washed, and finally dried by hot blast at 90 °C for 30 min. to obtain ASA powder particles having weatherability.

To the ASA powder particles having weatherability obtained by the method, a SAN (81HF) copolymer resin (LG CHEM. Ltd. product) was introduced as an antioxidant and a photostabilizer, and the whole was kneaded and extruded at 200 to 250 °C to prepare a pellet having a rubber content of 20 %. The pellet was injection molded again and the properties were measured, and the results are shown in Table 1.

The properties were measured by the ASTM method, and measurement conditions of each property were as follows.

Izod impact strength: ASTM D256 (1/4" notched at 25 °C, unit: Kg · cm/cm)

colorability: decision made with the naked eye

surface gloss: ASTM D528 (45° angle)

[Example 2]

ASA resin was prepared by the same method as in Example 1, except
5 that the amount of styrene used in the first polymerization step was increased to 5
wt parts, and the amount of styrene used in the third polymerization step was
reduced to 35 wt parts. The properties were measured by the same method as
in Example 1, and the results are shown in Table 1.

[Example 3]

10 ASA resin was prepared by the same method as in Example 1, except
that TBHP (t-butyl hydroperoxide) was used instead of cumene hydroperoxide as
the initiator in the second polymerization step. The properties were measured by
the same method as in Example 1, and the results are shown in Table 1.

[Example 4]

15 ASA resin was prepared by the same method as in Example 1, except
that methylmethacrylate was used instead of the styrene monomer in the first
polymerization step. The properties were measured by the same method as in
Example 1, and the results are shown in Table 1.

[Example 5]

20 ASA resin was prepared by the same method as in Example 1, except
that acrylonitrile was used instead of the styrene monomer in the second

polymerization step. The properties were measured by the same method as in Example 1, and the results are shown in Table 1.

[Comparative Example 1]

ASA resin was prepared by the same method as in Example 1, except
 5 that methylmethacrylate and the styrene monomer were not added in the second polymerization step, and the amounts thereof were added in the third step polymerization. The properties were measured by the same method as in Example 1, and the results are shown in Table 1.

[Comparative Example 2]

10 ASA resin was prepared by the same method as in Example 1, except that potassium persulfate (KPS) as a water-soluble initiator was used instead of cumene hydroperoxide (CHP) in the second and third polymerization steps. The properties were measured by the same method as in Example 1, and the results are shown in Table 1.

15 [Table 1]

	Examp e 1	Examp e 2	Examp e 3	Examp e 4	Examp e 5	Com. Exam. 1	Com. Exam. 2
Impact strength (Kg · cm/cm)	20	16	19	20	18	12	10
Surface gloss (45°)	99	101	95	93	95	80	75
Colorability	good	good	good	good	good	Bad	Very bad

As shown in Table 1, Examples 1 to 5 using both a water-soluble initiator and an oil-soluble initiator of the present invention had excellent impact strength at 16 ~ 20 Kg · cm/cm, and surface gloss and colorability were very excellent. On the other hand, Comparative Examples 1 and 2 used only a water-soluble initiator, and the thus-produced ASA resin had a very low impact strength, and colorability was extremely bad.

As explained, the method of preparing a thermoplastic resin of the present invention results in a resin with superior impact resistance, chemical resistance, and processability, etc., and particularly a thermoplastic resin with good weatherability and having improved colorability and surface gloss can be obtained.

WHAT IS CLAIMED IS :

1. A method for preparing a weatherable thermoplastic resin comprising the steps of:

- a) preparing a seed by adding 0.05-0.2 weight parts of a water-soluble initiator to 0.5-10 weight parts of either an aromatic vinyl compound or a (meth)acrylic acid alkyl ester, and polymerizing;
- b) preparing an alkyl acrylate rubber polymer by adding
 - i) 5-45 weight parts of an alkyl acrylate monomer,
 - ii) 1-5 weight parts of an aromatic vinyl compound, a (meth)acrylic acid alkyl ester, or a vinyl cyanide compound,
 - iii) 0.2-1.0 weight parts of a metal salt derivative of alkyl sulfosuccinate with $C_{12} \sim C_{18}$, or a metal salt derivative of alkyl sulfuric acid ester or metal salts of sulfonate with $C_{12} \sim C_{20}$, as an emulsifier, and
- iv) 0.05-2 weight parts of an oil-soluble initiator to the seed, and polymerizing; and
- c) preparing a thermoplastic resin by adding
 - i) 10-40 weight parts of an aromatic vinyl compound,
 - ii) 1-20 weight parts of a vinyl cyanide compound,
 - iii) 0.5-3.0 weight parts of metal salts of rosinate or metal salts of carboxylate with $C_{12} \sim C_{20}$, as an emulsifier, and

iv) 0.05-0.2 weight parts of an oil-soluble initiator

to the alkyl acrylate rubber polymer, and graft copolymerizing.

2. The method for preparing a weatherable thermoplastic resin according to Claim 1, wherein the alkyl acrylate rubber polymer obtainable in step b) has a diameter of 2500 ~ 5000 Å and a polymer aqueous solution thereof has pH of 5 ~ 9; and wherein the graft copolymer obtainable in step c) has a particle size of 3000 ~ 6000 Å and an aqueous solution thereof has pH of 8 ~ 11.

3. The method for preparing a weatherable thermoplastic resin according to Claim 1, wherein an aqueous solution of the emulsifier of step b) has pH of 3 ~ 9, and wherein an aqueous solution of the emulsifier of step c) iii) has pH of 9 ~ 13.

4. The method for preparing a weatherable thermoplastic resin according to Claim 1, wherein the water-soluble initiator of step a) is selected from the group consisting of potassium persulfate, sodium persulfate, and ammonium persulfate.

5. The method for preparing a weatherable thermoplastic resin according to Claim 1, wherein the oil-soluble initiator of step b) and step c) is cumene hydroperoxide, t-butyl hydroperoxide, or benzoyl peroxide.

6. The method for preparing a weatherable thermoplastic resin according to Claim 1, wherein the alkyl acrylate monomer of step b) is selected from the group consisting of butyl acrylate, ethyl acrylate, and methyl acrylate.

7. The method for preparing a weatherable thermoplastic resin according

to Claim 1, wherein the aromatic vinyl compound of step b) is selected from the group consisting of styrene, α -methyl styrene, and vinyl toluene.

8. The method for preparing a weatherable thermoplastic resin according to Claim 1, wherein the vinyl cyanide compound of step b) is acrylonitrile or
5 methacrylonitrile.

9. The method for preparing a weatherable thermoplastic resin according to Claim 1, wherein the (meth)acrylic acid alkyl ester of step b) is selected from the group consisting of (meth)acrylic acid methyl ester, (meth)acrylic acid ethyl ester, (meth)acrylic acid propyl ester, (meth)acrylic acid 2-ethyl hexyl ester,
10 (meth)acrylic acid decyl ester, and (meth)acrylic acid lauryl ester.

10. The method for preparing a weatherable thermoplastic resin according to Claim 1, wherein the polymerization reaction of step b) is performed while further comprising 0.01-0.07 weight parts of a grafting agent selected from the group consisting of v) aryl methacrylate (AMA), triarylisocyanurate (TAIC),
15 triarylamine (TAA); and diarylamine (DAA).

11. The method for preparing a weatherable thermoplastic resin according to Claim 1, wherein the polymerization reactions of step a) and step b) are each performed while further comprising a crosslinking agent selected from the group consisting of ethyleneglycol dimethacrylate, diethyleneglycol
20 dimethacrylate, triethyleneglycol dimethacrylate, 1,3-buthanediol dimethacrylate, 1,6-hexanediol dimethacrylate, neopentylglycol dimethacrylate, trimethylol

propane trimethacrylate, and trimethylol methane triarylate.

12. A weatherable thermoplastic resin prepared by the method of Claim 1.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR01/02274**A. CLASSIFICATION OF SUBJECT MATTER****IPC7 C08F 265/06**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 C08F 265/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KR 1999 - 60,688 A (KORYEO CHEMICALS CO.,LTD), 26 JULY 1999 (26.07.1999) SEE THE WHOLE DOCUMENT	1
A	KR 2000 - 55,262 A (JAEIL TEXTILE CO.,LTD), 05 SEPTEMBER 2000(05.09.2000) SEE THE WHOLE DOCUMENT	1
A	KR 2000 - 18,421 A (JAEIL TEXTILE CO.,LTD), 06 APRIL 2000(06.04.2000) SEE THE WHOLE DOCUMENT	1
A	JP 10-139,833 A (TECHNO POLYMER CO.,LTD), 26 MAY 1998 (26.05.1998) SEE THE WHOLE DOCUMENT	1
A	JP 11-236,414 A (ASAHI CHEM IND CO LTD.), 02 JULY 1992 (02.07.1992) SEE THE WHOLE DOCUMENT	1

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

03 APRIL 2002 (03.04.2002)

Date of mailing of the international search report

03 APRIL 2002 (03.04.2002)

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
Government Complex-Daejeon, 920 Dunsan-dong, Seo-gu,
Daejeon Metropolitan City 302-701, Republic of Korea
Facsimile No. 82-42-472-7140

Authorized officer

KIM, Jang Gang

Telephone No. 82-42-481-5544



Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR01/02274

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
KR 1999 - 60,688 A	26.07. 1999	NONE	
KR 2000 - 55,262 A	05.09. 2000	NONE	
KR 2000 - 18,421 A	06.04.2000	NONE	
JP 10-139,833 A	26.05.1998	NONE	
JP 11-236,414 A	02.07.1992	NONE	

Form PCT/ISA/210 (patent family annex) (July 1998)